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For presentation at the 9th International Workshop of Combustion & Propulsion – Energetic Materials in La Spezia, Italy, taking place 14-19 September 2003.

14. ABSTRACT

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Isolation of Boron and Carbon Atoms in Cryogenic Solids

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9th International Workshop on Combustion and Propulsion
NOVEL ENERGETIC MATERIALS AND APPLICATIONS
14-18 September 2003
Lerici, La Spezia, Italy

Outline

Theoretical Isp of cryogenic solid propellants composed of the atoms, dimers and trimers of lightweight elements isolated in solid para hydrogen. Consequences of condensation.

Spectroscopic studies of Boron/Carbon clusters by matrix isolation spectroscopy.

Development of stable, hi-flux boron atom source for preparation of cryogenic solid HEDM (under auspices of Small Business Innovative Research (SBIR) program.

First optical spectrum of B_3 (under auspices of International Research Initiative of the Air Force Office of Scientific Research).

Video of exploding B/C and C HEDM.

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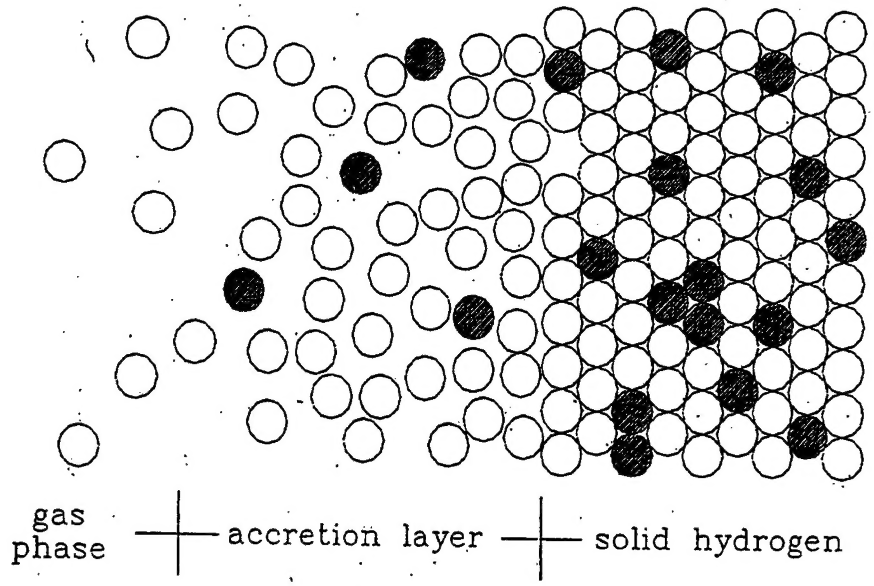
Cryosolid Propellants Approach (Make)

* Rapid vapor deposition of metal atom vapor and pre-cooled parahydrogen gas onto a liquid helium cooled substrate in vacuum.



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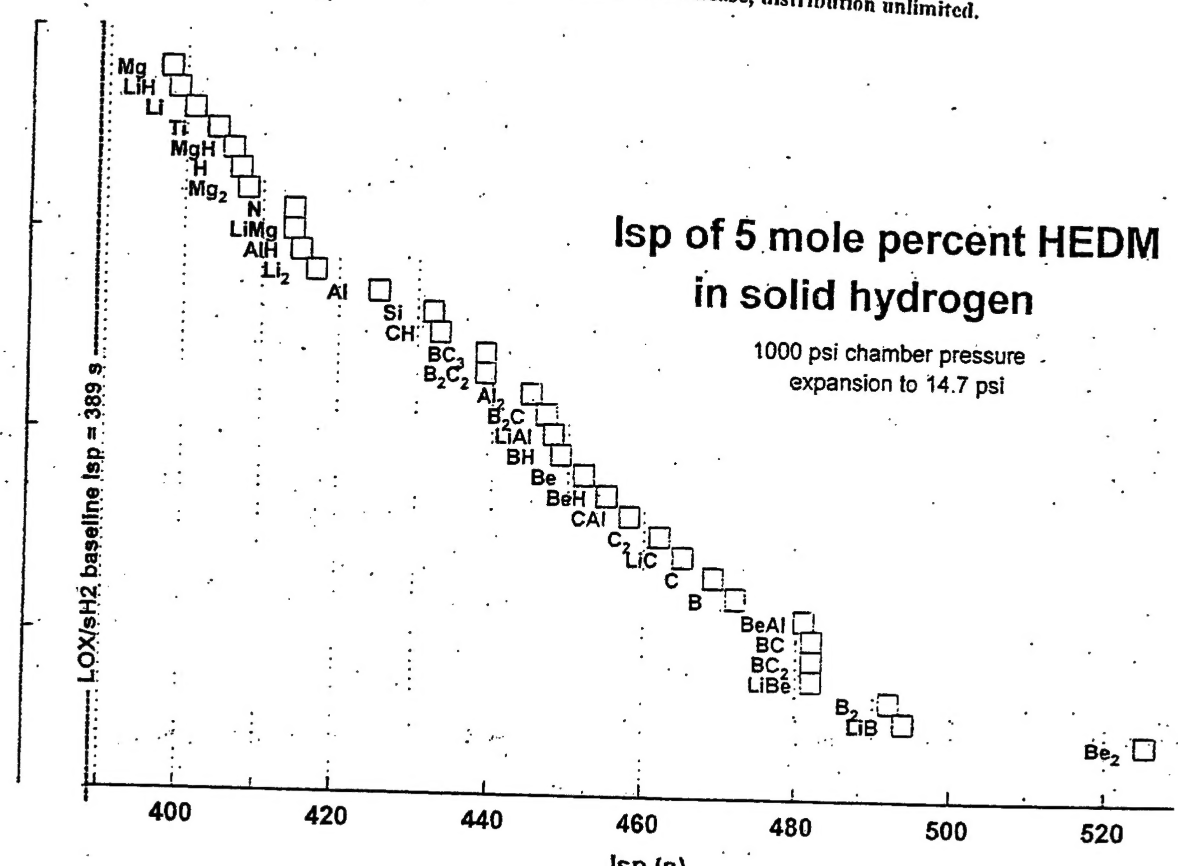

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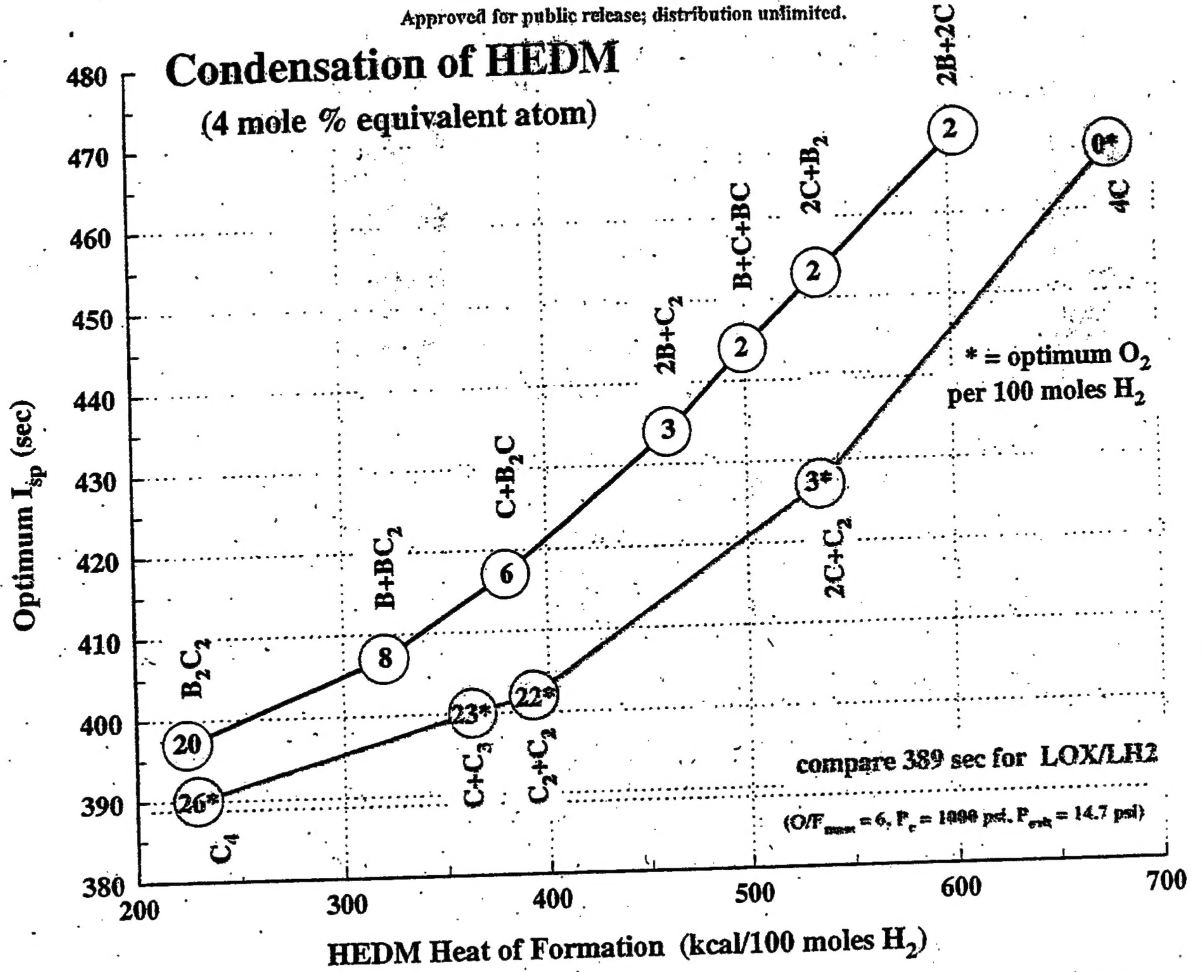
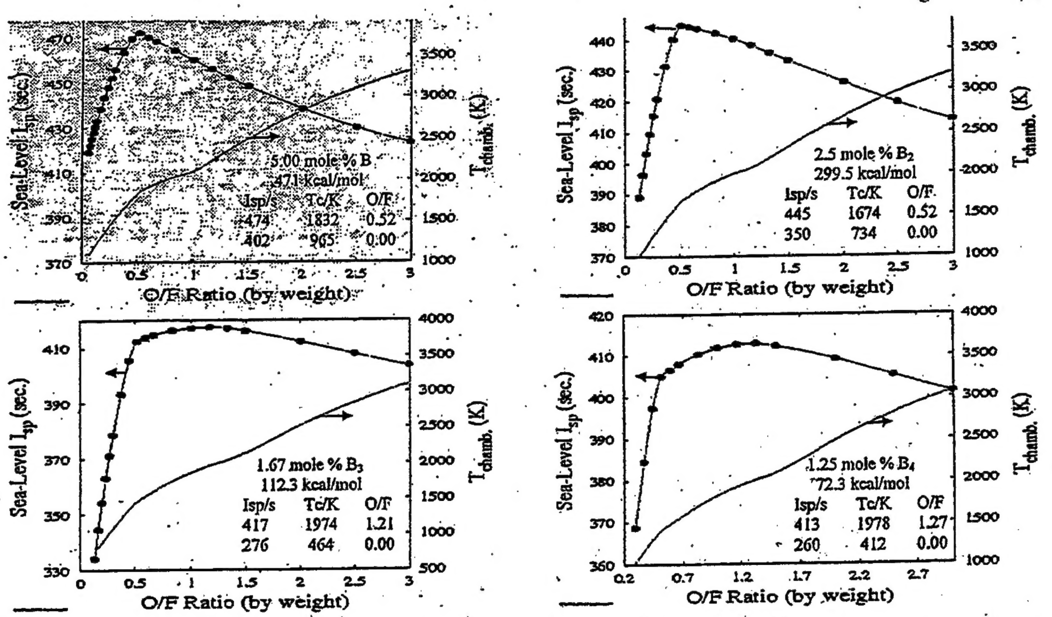
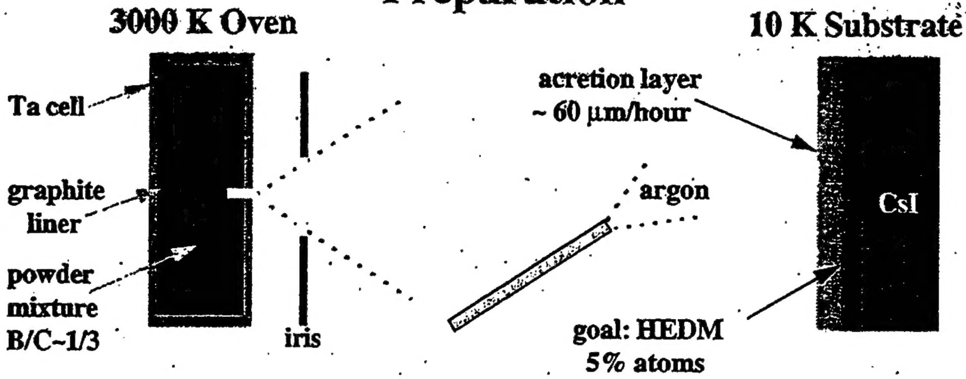




Optimization of boron HEDM propellant combustion with liquid oxygen.

The propellant formulation is $H_{190}B_5$, or 5 equivalent mole percent boron atoms isolated in 95 mole percent solid parahydrogen. The four panels show the optimization for each of four levels of atom condensation: (1) B atoms, (2) B_2 molecules, (3) B_3 molecules, and (4) B_4 molecules. The Isp and Tc were calculated for the Standard Rocket Condition: 1000 psi chamber pressure and expansion to sea level, which for LOX/LH2 produces an Isp of 389 s and a chamber temperature of 2984 K. The heats of formation for B_5H_{190} listed in each panel are derived from –2.20 kcal/mol for solid parahydrogen at 4.4 K, and 135.0 for B, 203.4 for B_2, 192.8 for B_3, and 225 kcal/mol for B_4. The Isp and Tc for no oxidizer are listed together with the optimum (maximum) Isp obtainable for the specified O/F ratio (by mass) and the value of Tc. In all cases the chamber temperature with boron HEDM is very much less than the Tc of the LOX/LH2 Standard Rocket, which produces Isp = 389 s with Tc = 2984. The uncondensed boron HEDM Isp of 474 s runs at 1832 K. With no oxidizer, the uncondensed boron HEDM rocket runs at 965 K and produces Isp = 402 s.

Preparation



Annealing

a0 10 K	a3 32.5 K, 60 s	a6 40.0 K, 20 s
a1 27.5 K, 120 s	a4 35.0 K, 45 s	sublimation
a2 30.0 K, 90 s	a5 37.5 K, 20 s	rate ~ 1 µm/s

Precision matched pair of matrices

Green Matrix	$^{11}B/^{10}B = 80/20$	enhanced $^{11}B_JC_{n-J}$
Red Matrix	$^{11}B/^{10}B = 27/73$	enhanced $^{10}B_JC_{n-J}$

GOAL - 5% atoms in matrix

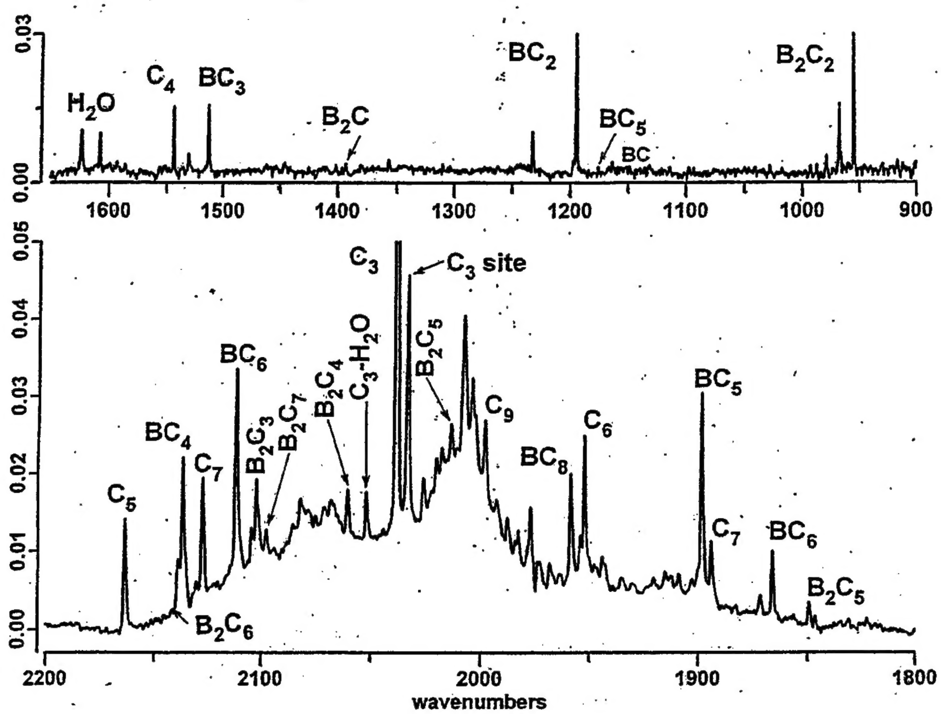
B_JC_{n-J}

Infrared Intensities km mol^{-1}

B3LYP/cc-pVDZ

Oven vaporization of B/C < 0.3
Argon Matrix/10 K Substrate
Annealing to Constant Composition
Isotopic Substitution & FTIR
Isotopomer Fingerprinting
Quantitative FTIR Analysis

n	cyclic	J = 0	1	2	3	4	5	6	7	8	9	10	11	12	13
1		C 0	B 0												
2		C_2 0	BC 43	B_2 0											
3		C_3 772	BC_2 112	B_2C 7	B_3 64										
4	cC_4 498	C_4 291	BC_3 153	B_2C_2 1004	B_3C 55	B_4									
5		C_5 2540	BC_4 2362	B_2C_3 2435	B_3C_2	B_4C	B_5								
6	cC_6 808	C_6 1074	BC_5 768	B_2C_4 1019	B_3C_3	B_4C_2	B_5C	B_6							
7		C_7 4662	BC_6 4356	B_2C_5 4967	B_3C_4	B_4C_3	B_5C_2	B_6C	B_7						
8	cC_8 1072	C_8 1990	BC_7 1612	B_2C_6 1593	B_3C_5	B_4C_4	B_5C_3	B_6C_2	B_7C	B_8					
9		C_9 6562	BC_8 6187	B_2C_7 5804	B_3C_6	B_4C_5	B_5C_4	B_6C_3	B_7C_2	B_8C	B_9				
10	cC_{10} 882	C_{10} 2836	BC_9	B_2C_8	B_3C_7	B_4C_6	B_5C_5	B_6C_4	B_7C_3	B_8C_2	B_9C	B_{10}			
11		C_{11} 15171	BC_{10}	B_2C_9	B_3C_8	B_4C_7	B_5C_6	B_6C_5	B_7C_4	B_8C_3	B_9C_2	$B_{10}C$	B_{11}		
12	cC_{12} 1504	C_{12} 4798	BC_{11}	B_2C_{10}	B_3C_9	B_4C_8	B_5C_7	B_6C_6	B_7C_5	B_8C_4	B_9C_3	$B_{10}C_2$	$B_{11}C$	B_{12}	
13		C_{13} 21421	BC_{12}	B_2C_{11}	B_3C_{10}	B_4C_9	B_5C_8	B_6C_7	B_7C_6	B_8C_5	B_9C_4	$B_{10}C_3$	$B_{11}C_2$	$B_{12}C$	B_{13}



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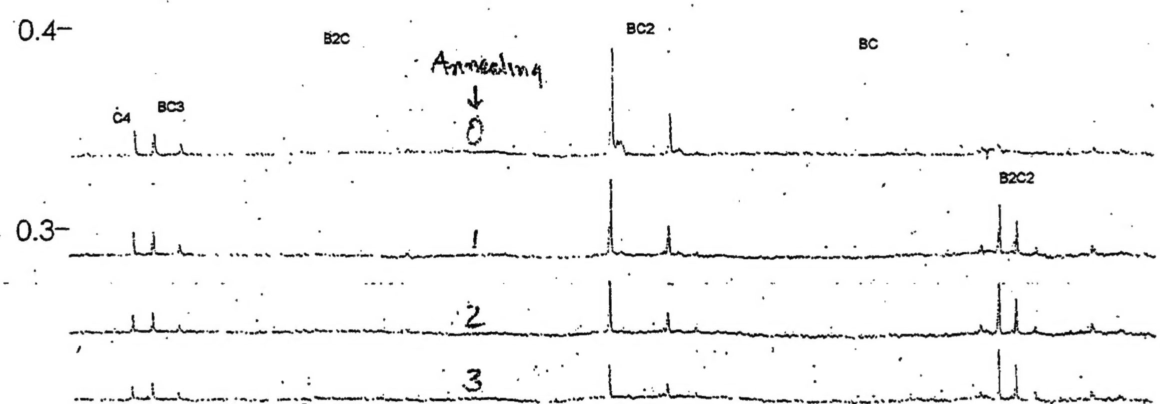
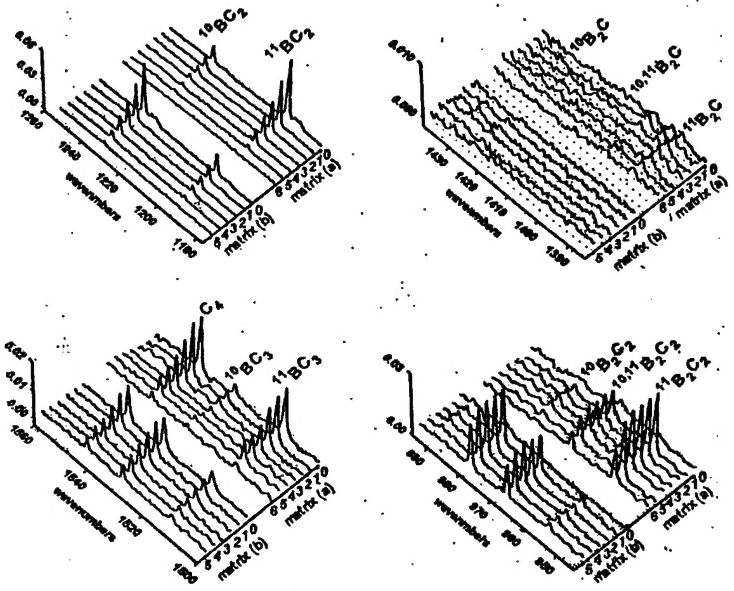


Survey spectra showing BC_2, B_2C, C_4, BC_3, B_2C_2

Doublet peaks belonging to $^{10}BC_{n-1}$ and $^{11}BC_{n-1}$ and triplets belonging to $^{10}B_2C_{n-2}$, $^{10,11}B_2C_{n-2}$, and $^{11}B_2C_{n-2}$ are seen with inverted intensity ratios. Note red shift of BC_3 from C_4. BC, B_3, and B_3C were not observed.



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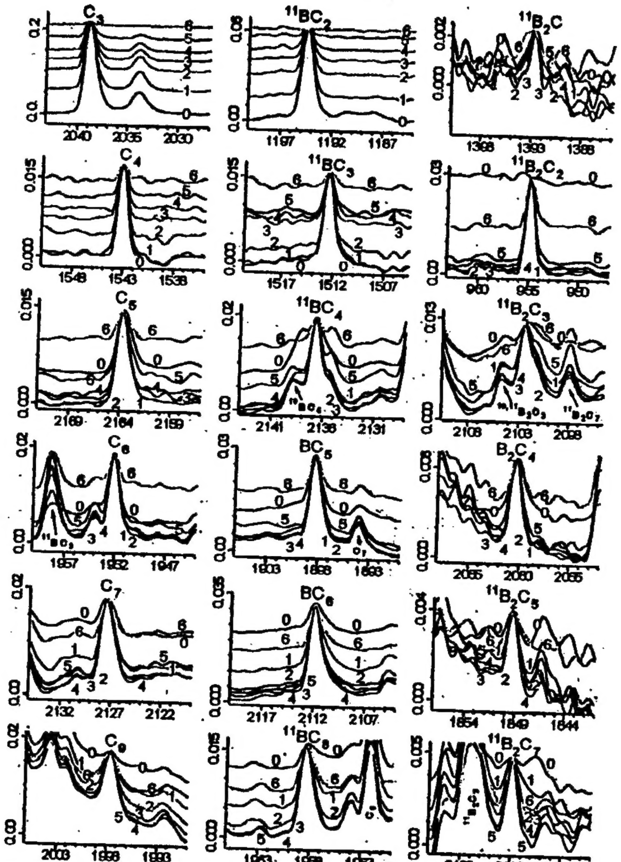

Figure 2. Annealing behaviors of B_jC_{n-j} species in matrix (a). Spectra labeled '0' were obtained from the originally deposited matrix, and spectra labeled '1' to '6' were obtained after successive annealings as detailed in the Fig. 1 caption. Absolute absorbance scales, $A_{exp} = -\log_{10}\tau$, are offset to force coincidence at the peak maxima. Boron isotopomers of BC_5, BC_6 and B_2C_4 are unresolved. The weaker of two bands of B_2C_5 (I_{theory} = 1034 km mol^{-1}, at 1850 cm^{-1}) is shown here. Spectral resolution is limited to ~1 cm^{-1} by matrix broadening.

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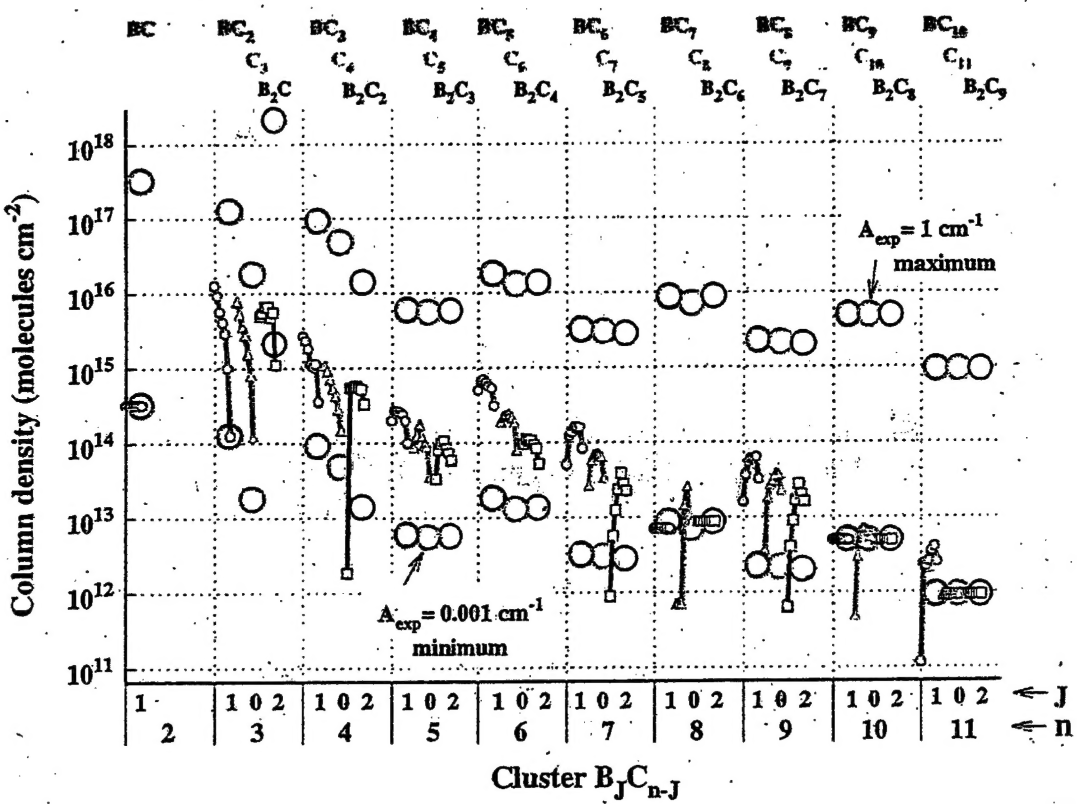

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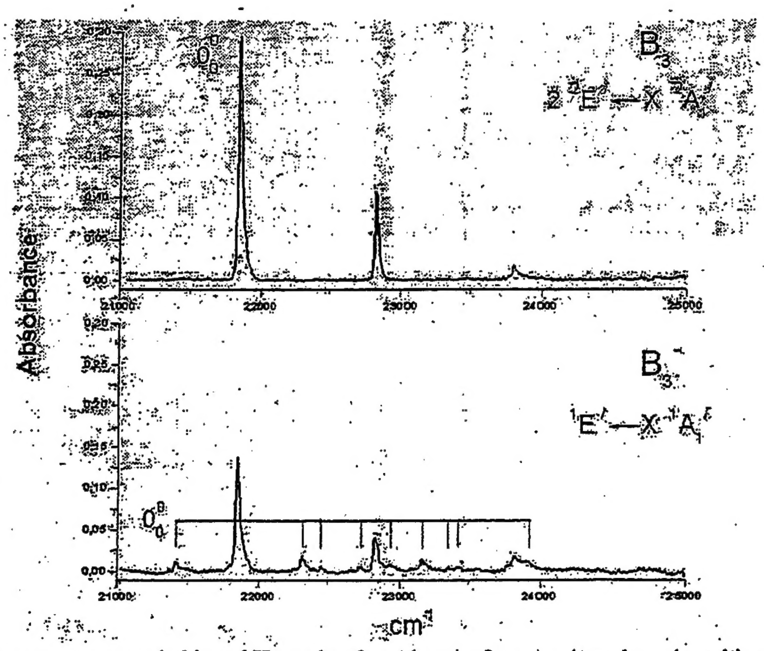

Electronic absorption spectra recorded in a 6 K matrix after 4 hours of mass-selected co-deposition of B_3^- with neon. The bottom trace shows the $^1E'$ - X $^1A_1'$ electronic transition of B_3^- overlapped by the 2 $^2E'$ - X $^2A_1'$ system of B_3, produced from partial neutralization of the anions impinging on the matrix during deposition. The top trace reveals the 2 $^2E'$ - X $^2A_1$ electronic transition of B_3 measured after exposure to UV radiation. Absorption belonging to the anion disappears.

M. Wyss, E. Riaplov, A. Batalov, J. P. Maier, T. Weber, W. Meyer, P.Rosmus, *J. Chem. Phys.* (2003, in press).
University of Basel, University of Kaiserslautern, Université de Marne la Vallée

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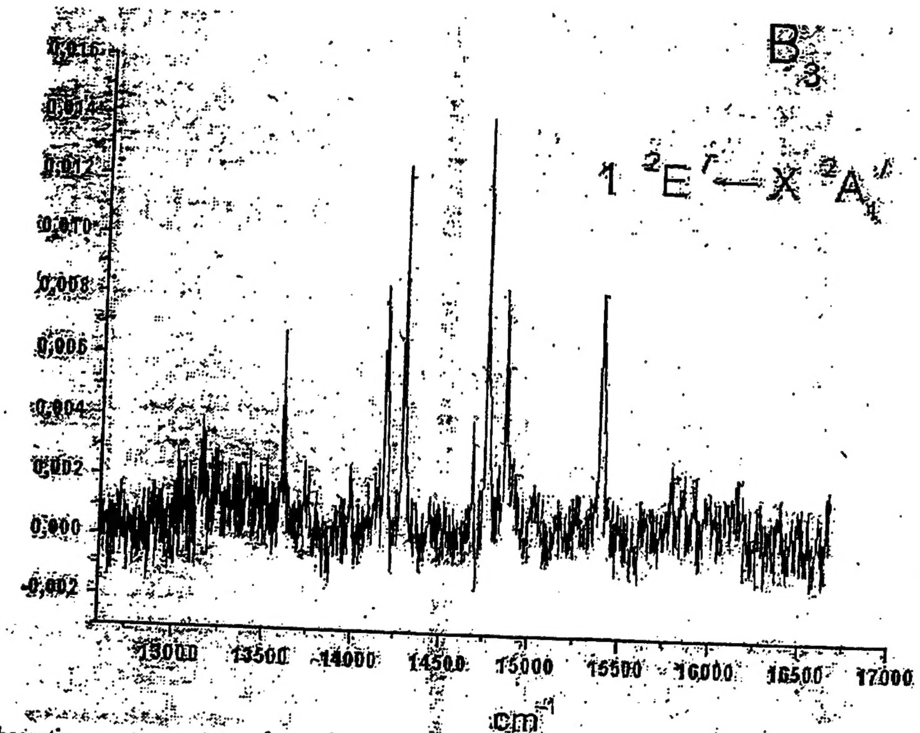

Electronic absorption spectrum of the $1\ ^2E' - X\ ^2A_1'$ electronic transition of B_3 recorded after 4 hours of mass-selected co-deposition with neon followed by UV irradiation of the 6 K matrix.

M. Wyss, E. Riaplov, A. Batalov, J. P. Maier, T. Weber, W. Meyer, P. Rosmus, *J. Chem. Phys.* (2003, in press).
University of Basel, University of Kaiserslautern, Université de Marne la Vallée

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AFRL-PR-ED-TR-2003-0030

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Advanced Rocket Propulsion Technologies Boron Vapor Source for HEDM

Paul C. Nordine

Containerless Research Inc.
906 University Place
Evanston IL 60201-3149

June 2003

SBIR Phase I Final Report

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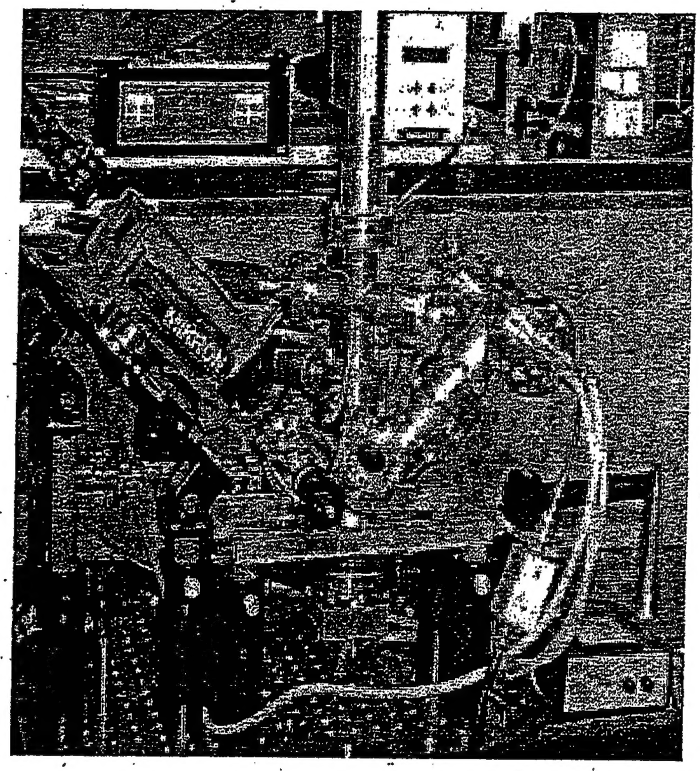

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Conclusions

Large Isp improvements are produced by cryogenic solid propellants with atoms, dimers, trimers, and tetramers isolated in solid hydrogen, but condensation leads to loss of benefit.

5 mole percent B atoms produces Isp of 474 seconds compared to 389 s for LOX/sH2 . The HEDM combustion temperature is 1832 K, compared to 2984 K for LOX/sH2.

Annealing kinetics of disappearance of C_3 and BC_2, and of appearance of B_2C, C_4, BC_3, B_2C_2, C_5, BC_4, and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix.

~80% or more of the initially deposited HEDM existed as atoms, dimers and trimers.

B_2C_n molecules are linear, with boron atoms attached to each end, and are immune to radical attack and condensation during annealing.

Theory predicts that a 12 kcal/mol barrier exists for B atom insertion into H_2, so isolation by co-condensation may be possible.

A stable, high-flux B-atom source has been developed under the Small Business Innovative Research Program capable of production of 100 mg of Boron HEDM in a few hours.

B_2 or B_3 may be the ultimate sinks (islands of stability) for atoms in the low temperature environment.

Studies of the spectroscopy and reactivity of B atoms and small clusters with hydrogen are underway at the University of Basel, supported by the Air Force Office of Scientific Research through the International Research Initiative program.

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BACKUP CHARTS

Species	ΔH_f	[illegible]	% LOX	[illegible]	% M	% LOX	% sH_2
H_2 (s)	-2.21	—	—	389	0	20.6	79.4
H	52.1	707	19.0	1478	100.0	0	0
LiH	34.2	399	13.1	476	20.4	5.1	79.6
BeH	82.4	355	2.8	551	15.2	7.6	84.8
BH	109.3	449	3.8	568	28.3	0	71.7
CH	143.2	339	2.2	609	24.8	0	75.2
MgH	55.7	306	14.9	438	14.0	7.0	86.0
AlH	61.2	315	10.1	445	11.1	8.4	88.9
Li	38.1	307	12.2	381	19.9	5.0	80.1
Li_2	53.6	367	5.8	461	11.6	5.8	88.4
LiBe	109.8	482	3.9	512	15.0	7.6	85.0
LiB	159.6	494	5.0	527	29.0	0	71.0
LiC	159.9	465	1.3	523	30.0	0	70.0
LiMg	69.3	411	5.8	432	8.3	6.2	91.7
LiAl	97.4	448	5.0	458	7.3	7.4	92.7
Be	77.4	352	2.5	541	14.4	7.2	85.6
Be_2	153.1	525	5.0	545	7.8	7.8	92.2
BeAl	147.4	381	6.3	485	6.2	7.7	93.8
B	135.0	372	3.8	507	23.0	0	77.0
B_2	207.2	492	7.4	550	14.3	0	85.7
BC	201.6	482	3.7	542	14.2	0	85.8
C	171.3	469	0.0	645	20.0	0	80.0
C_2	199.3	462	0.0	533	15.3	0	84.7
CAl	174.5	458	3.8	464	6.8	5.1	93.2
N	113.0	511	15.0	581	34.2	0	65.8
Mg	35.2	398	16.8	317	13.8	7.1	86.2
Mg_2	68.8	408	8.9	416	7.4	7.6	92.6
Al	78.9	425	7.5	456	10.2	7.7	89.8
Al_2	125.1	445	7.5	445	5.6	8.4	94.4
Si	107.6	432	5.1	451	8.2	8.2	91.8
Ti	113.2	404	11.5	414	9.0	7.9	91.0

Conditions: Chamber Pressure = 1000 psi, Exhaust Pressure = 14.7 psi

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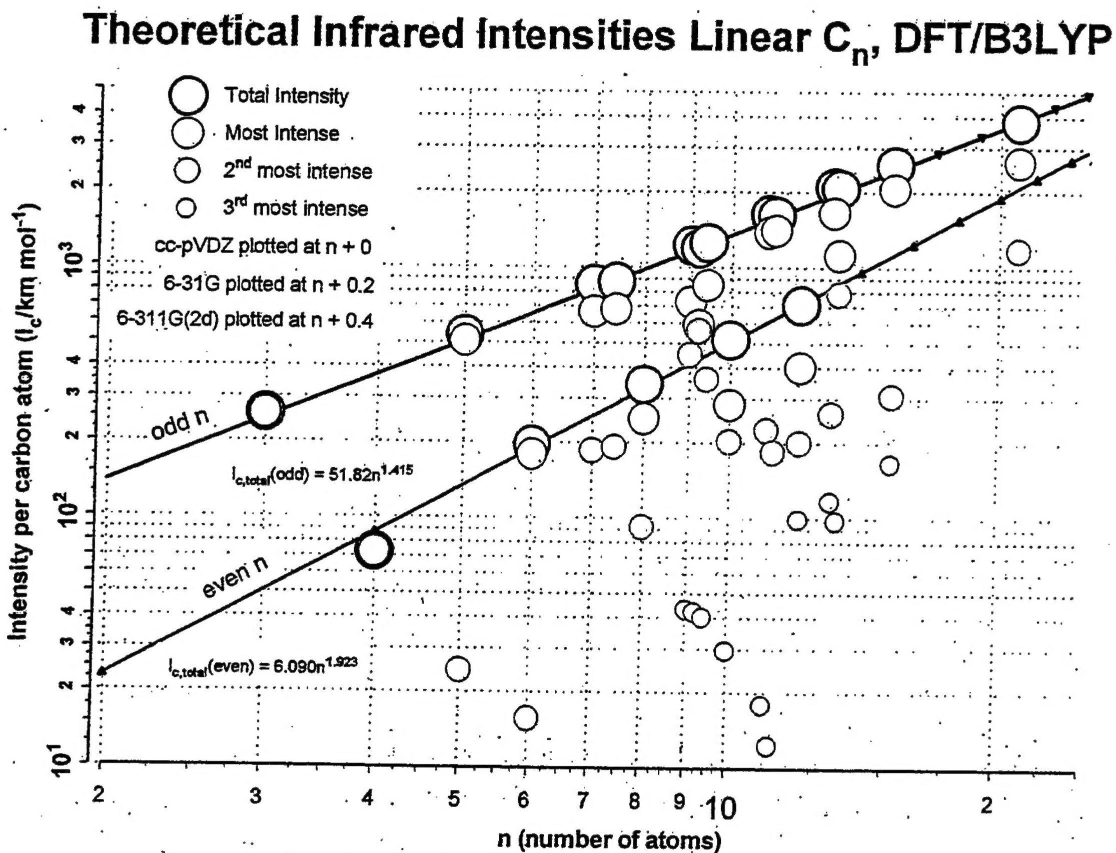

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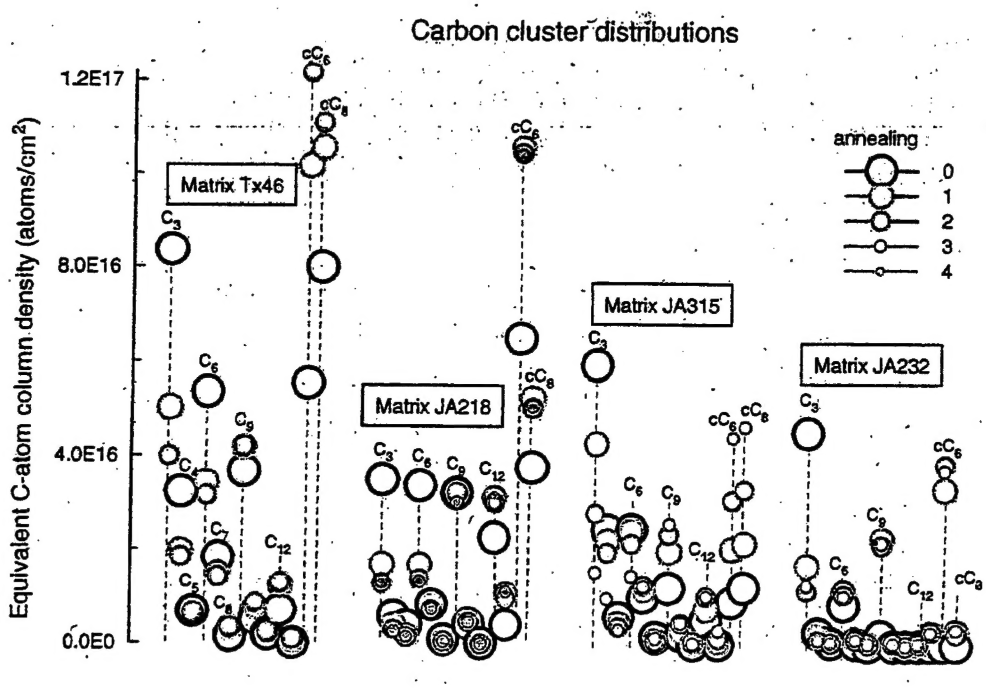

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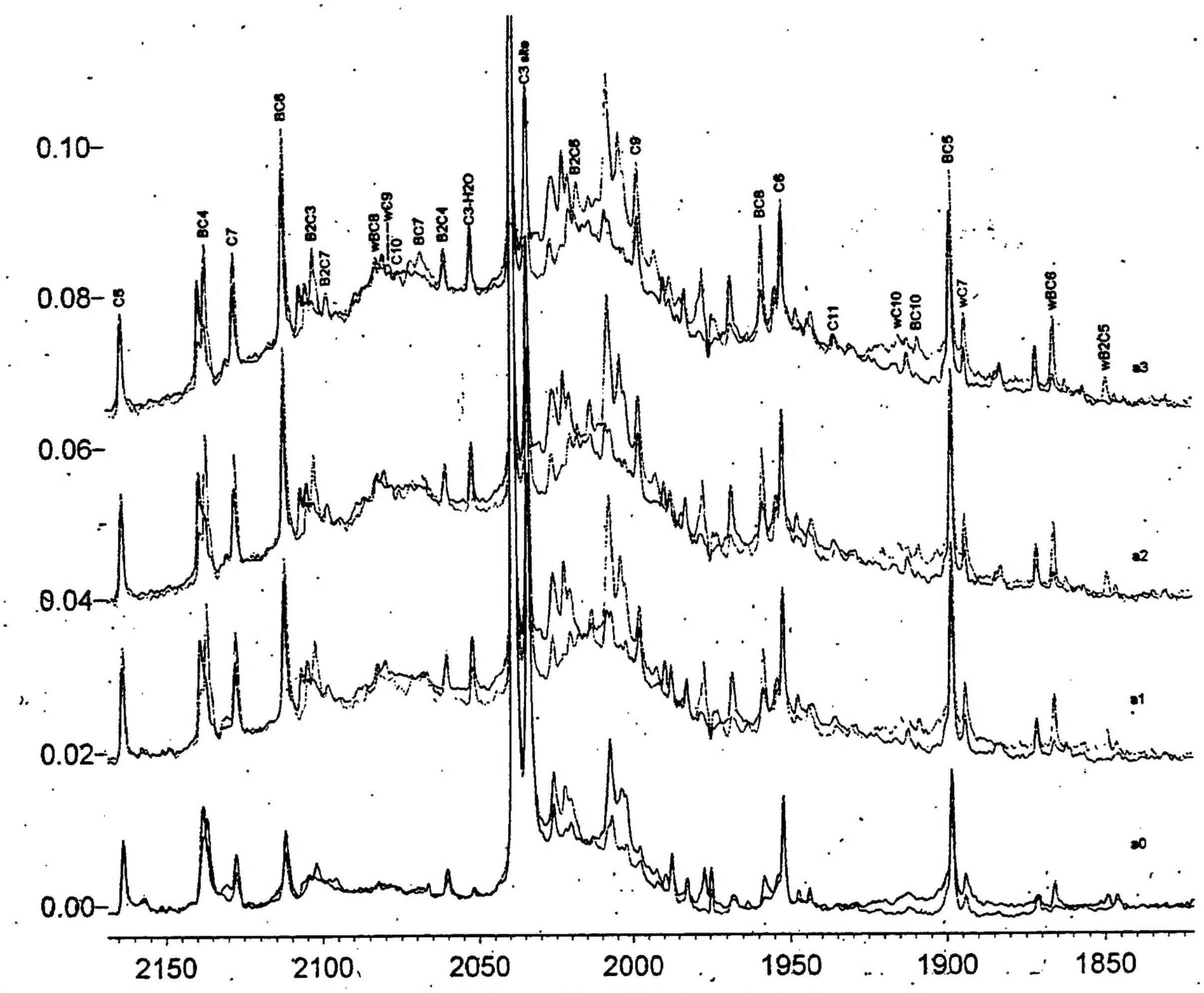
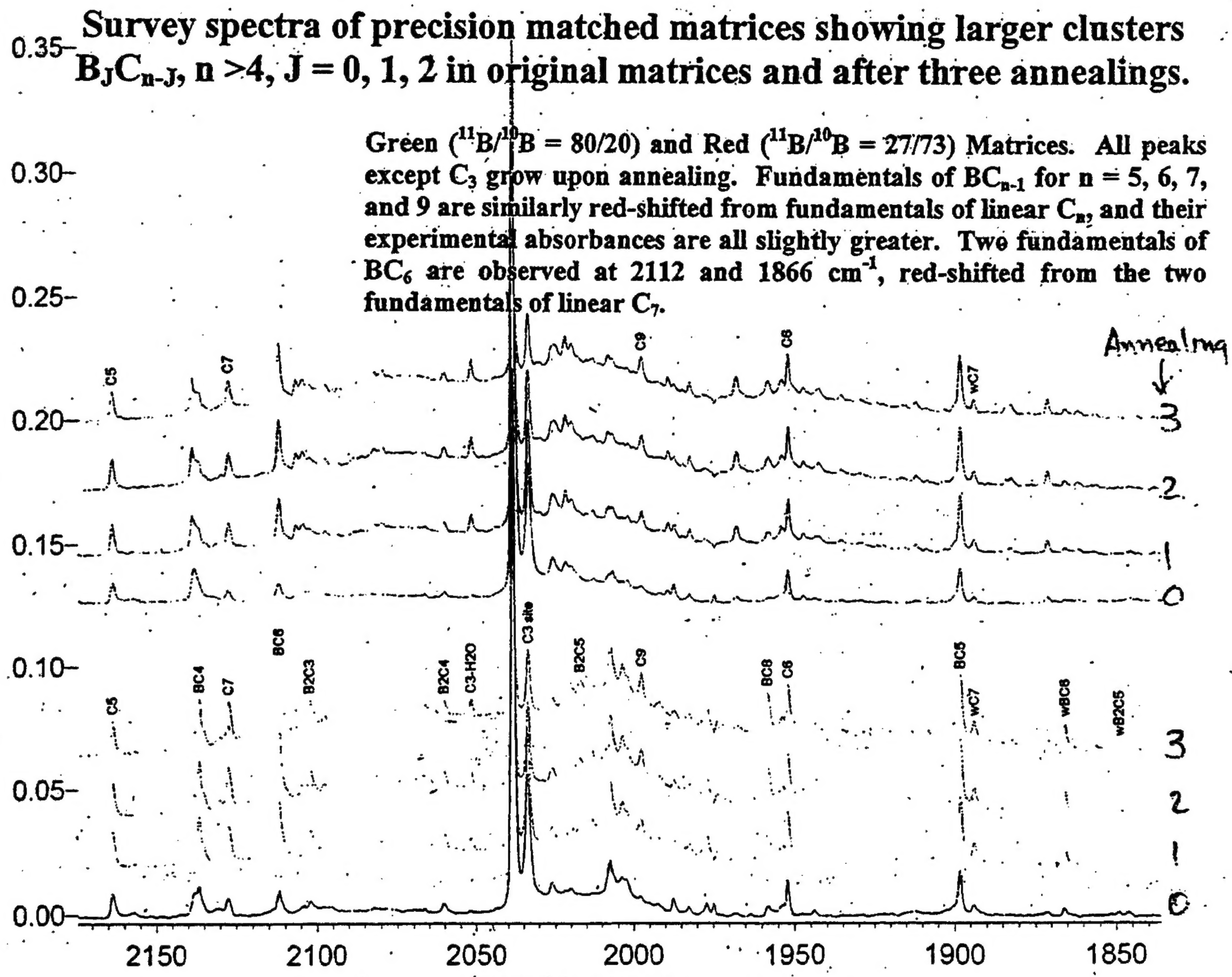


Survey spectra of precision matched matrices showing larger clusters B_JC_{n-J}, n >4, J = 0, 1, 2 in original matrices and after three annealings.

Green ($^{11}B/^{10}B$ = 80/20) and Red ($^{11}B/^{10}B$ = 27/73) Matrices. All peaks except C_3 grow upon annealing. Fundamentals of BC_{n-1} for n = 5, 6, 7, and 9 are similarly red-shifted from fundamentals of linear C_n, and their experimental absorbances are all slightly greater. Two fundamentals of BC_6 are observed at 2112 and 1866 cm^{-1}, red-shifted from the two fundamentals of linear C_7.



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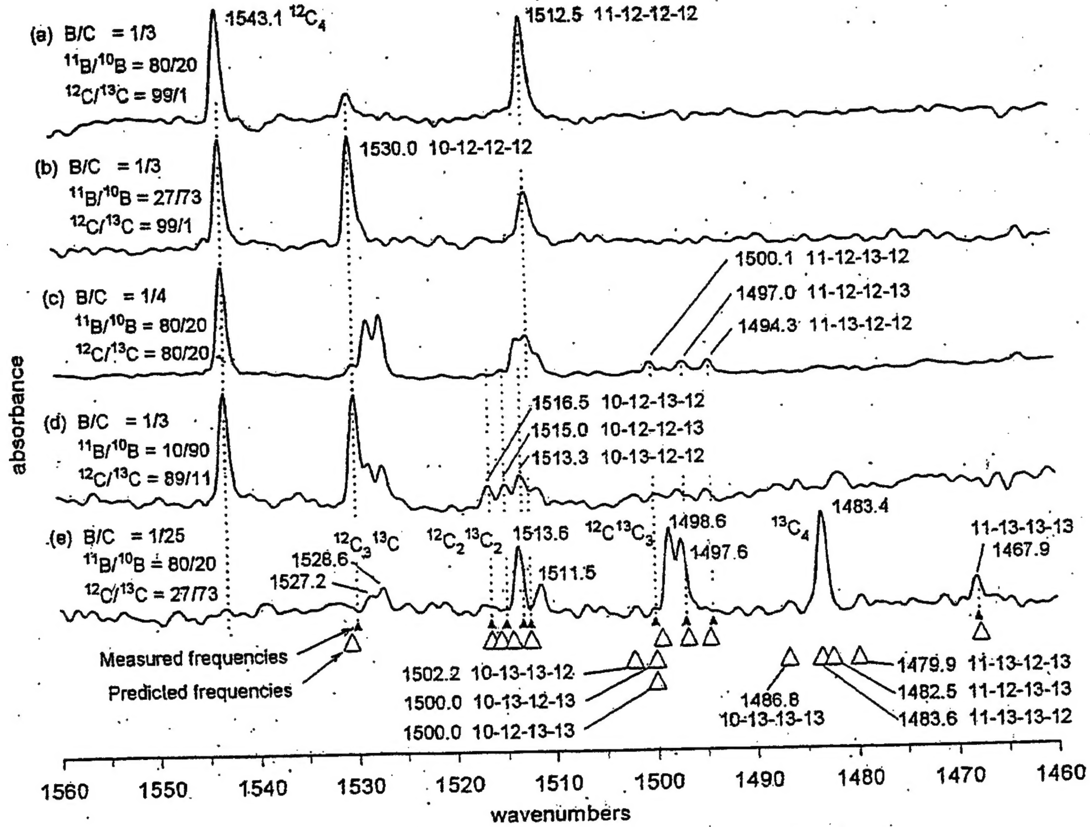
Identification of 9 of the 16 isotopomers of linear BCCC in 5 matrices.



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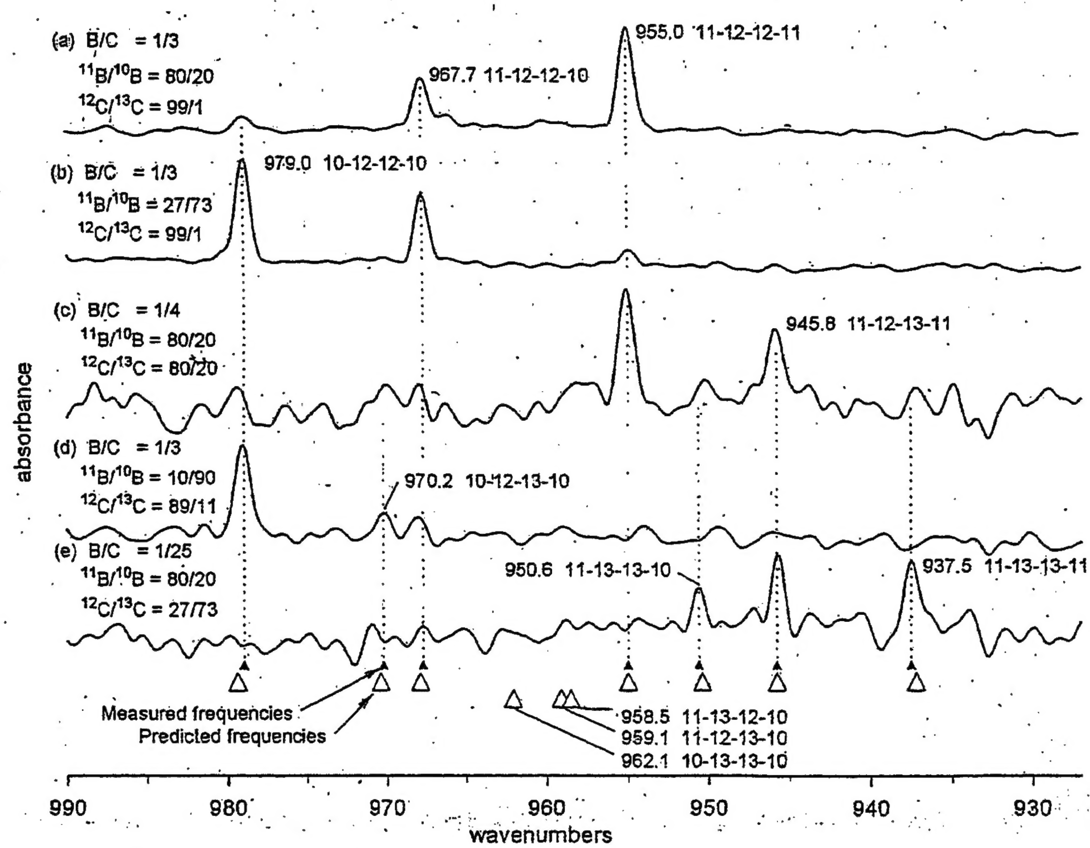
Identification of 7 isotopomers of the 10 isotopomers of BCCB in 5 matrices.



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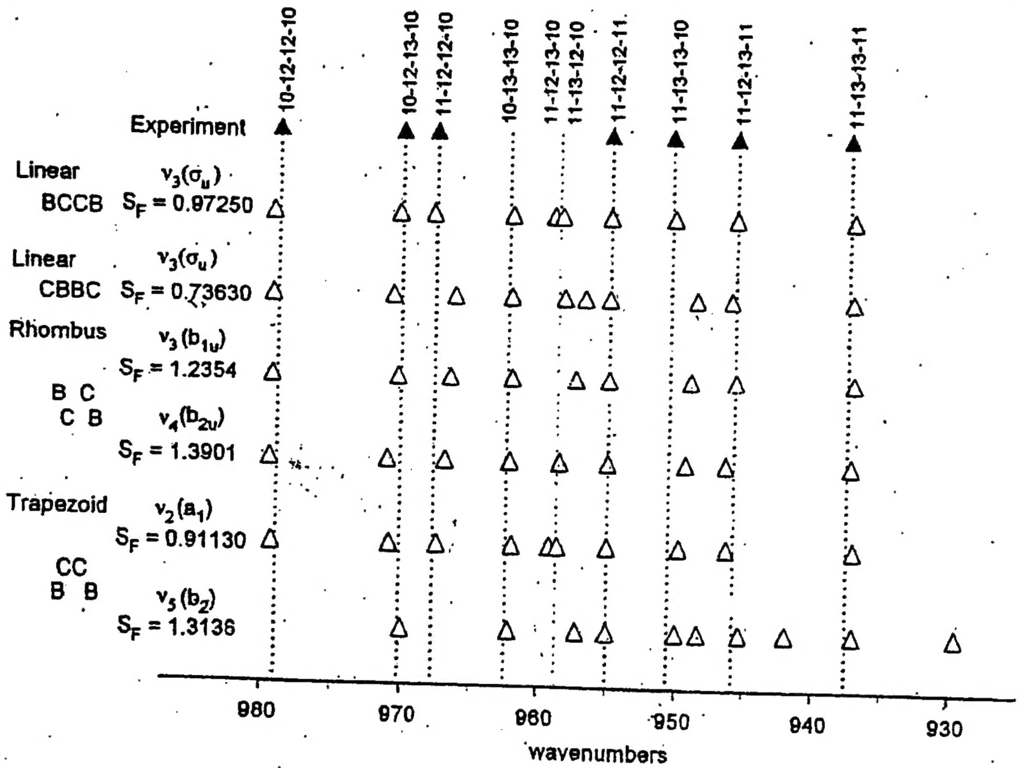
Four minimum energy geometries of B_2C_2 produce similar isotopomer fingerprints.
Scale factor (S_F = measured frequency/theoretical frequency) of linear BCCB = 0.97250.



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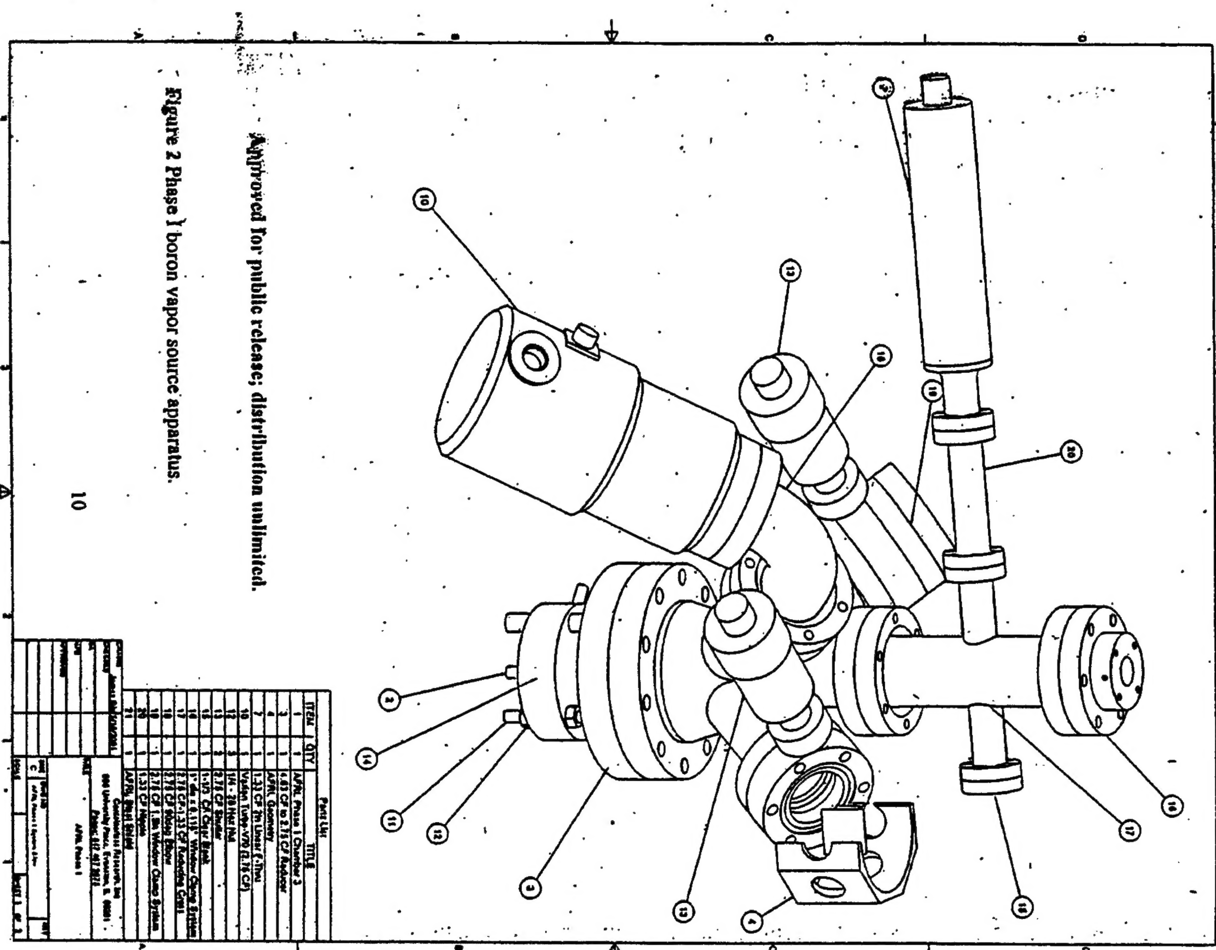

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Figure 2 Phase I boron vapor source apparatus.